



Final Scientific Report

Cover Page

BARD Project Number: IS4353-10

Title:

Interactions of engineered nanoparticles with dissolved organic matter (DOM) and organic
contaminants in water

Investigators:

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Keywords *not* appearing in the title and in order of importance. Avoid abbreviations.

Carbon nanotubes, Adsorption, Desorption, Colloidal stability, Environmental fate, Human health risk.

Abbreviations commonly used in the report, in alphabetical order:

Carbon nanotube (CNT), Dissolved organic matter (DOM), Hydrophobic organic contaminant (HOC).

Budget: IS: \$ 166,000

US: \$ 134,000

Total: \$ 300,000

Signature
Principal Investigator

Signature
Authorizing Official, Principal Institution



Final Scientific Report

Publication Summary (numbers)

	Joint IS/US authorship	US Authors only	Israeli Authors only	Total
Refereed (published, in press, accepted) BARD support acknowledged	3	6	1	10
Submitted, in review, in preparation	1			1
Invited review papers				
Book chapters				
Books				
Master theses			1	1
Ph.D. theses				
Abstracts				
Not refereed (proceedings, reports, etc.)				

Postdoctoral Training: List the names and social security/identity numbers of all postdocs who received more than 50% of their funding by the grant.

1. Dr. Adi Oren

Cooperation Summary (numbers)

	From US to Israel	From Israel to US	Together, elsewhere	Total
Short Visits & Meetings	1	1	1	3
Longer Visits (Sabbaticals)				

Description of Cooperation:

The proposed research was conducted in close collaboration between the two PIs. Dr. Chefetz and Dr. Xing have met a few times during the project for active discussions and planning for optimal flow of the project. Samples were exchanged between the two groups for analyses. The two groups were actively communicating for data analyses and the writing of scientific papers. In addition to the active and fruitful collaboration of the PIs in this project, students from the two groups communicated via emails to examine lab procedures, share and analyze experimental data.



Abstract

Background: Engineered carbon nanotubes (CNTs) are expected to be increasingly released into the environment with the rapid increase in their production and use. The discharged CNTs may interact with coexisting contaminants and subsequently change environmental behaviors and ecological effects of both the CNTs themselves and the contaminants. Dissolved organic matter (DOM) plays a critical role in the transport of CNTs in the aquatic environment, affecting both CNT's surface properties through adsorption, and its colloidal stability in solution. Therefore, CNT-bound DOM complexes may interact with coexisting contaminants, thus affecting their environmental fate. With increasing production and use of CNTs, there is an increasing risk that humans could be exposed to CNTs mainly through ingestion and inhalation. Since CNTs can be carriers of contaminants due to their high adsorption affinity and capacity, the distribution of these nanoparticles in the environment holds a potential environmental and health risk.

Project objectives: The overall goal of this project was to gain a better understanding of the environmental behavior of engineered nanoparticles with DOM and organic pollutant in aqueous systems. The scope of this study includes: characterizing various types of engineered nanoparticles and their interaction with DOM; binding studies of organic contaminants by nanoparticles and DOM-nanoparticle complexes; and examining interactions in DOM-nanoparticles-contaminant systems.

Major conclusions, solutions and achievements: DOM has a pronounced effect on colloidal stability of CNTs in solution and on their surface chemistry and reactivity toward associated contaminants. The structure and chemical makeup of both CNTs and DOM determine their interactions and nature of formed complexes. CNTs, contaminants and DOM can co-occur in the aquatic environment. The occurrence of co-contaminants, as well as of co-introduction of DOM, was found to suppress the adsorption of organic contaminants to CNTs through both competition over adsorption sites and direct interactions in solution. Furthermore, the release of residual contaminants from CNTs could be enhanced by biomolecules found in the digestive as well as the respiratory tracts, thus increasing the bioaccessibility of adsorbed contaminants and possibly the overall toxicity of contaminant-associated CNTs. Contaminant desorption could be promoted by both solubilization and sorptive competition by biological surfactants.

Scientific and agricultural implications: The information gained in the current project may assist in predicting the transport and fate of both CNTs and associated contaminants in the natural environment. Furthermore, the results imply a serious health risk from contaminant-associated CNTs.



Achievements

Dissolved organic matter (DOM) of various types (humic, fulvic and tannic acids) was found to have a pronounced effect on colloidal stability of fullerene nanoparticles (C60) in solution. The molecular weight of DOM positively affected, while its polarity negatively affected colloidal stability of the nanoparticles. Increasing Ca^{2+} concentration enhanced nanoparticles aggregation (Mashayekhi et al., 2012). The interaction of C60 nanoparticles with reference compounds of DOM was computationally simulated, indicating that DOM compounds were electron acceptors in the C60-DOM complexes. Thermodynamic calculations indicated that electrostatic interaction was the dominant driving force for the C60-DOM complexation process in water, increasing nanoparticles' apparent water solubility (Wang et al., 2011a). Adsorption of dissolved humic acids (HAs) by multi-walled carbon nanotubes (MWCNTs) was found to be driven mainly by the van der Waals force between alkyl components in HA and the MWCNTs. Adsorption intensity of HAs by MWCNTs depended on the latter's surface area and overall pore volume. Such information may help predict the transport and fate of both MWCNTs and organic contaminants and heavy metals associated with these sorbents in the natural environment (Wang et al., 2011b). Lin et al. (2012) showed that MWCNT surface-bound HA had higher adsorption capacity for Pb^{2+} than solid HA particles, conceivably because the surface-coating process could change structural conformation of HA, exposing more polar functional groups into the aqueous phase for complexation with Pb^{2+} . MWCNT-surface-bound HA introduced oxygen containing functional groups and negative charges on the MWCNTs, thus increasing Pb^{2+} adsorption on MWCNTs.

With increasing production and use of CNTs, there is an increasing risk that humans could be exposed to ingesting them. CNTs can be carriers of hydrophobic organic contaminants (HOCs) because of their high adsorption affinity and capacity. When used in adsorption filters for removal of contaminants from drinking water, trace amounts of HOCs could remain on CNTs in the water after the treatment, and enter the human gastrointestinal tract along with CNTs. Specifically, polycyclic aromatic hydrocarbons (PAHs) are important byproducts in CNT synthesis and their adsorption by CNTs can alter their fate, mobility and bioavailability. An in-vitro gastrointestinal tract model was used to simulate the digestion of PAH-adsorbed CNTs in the gastrointestinal tract. Adsorption of phenanthrene on CNTs was suppressed in pepsin (800 mg/L) solution (gastric) and bile salt (500 and 5000 mg/L) fluids (intestinal). In addition to competitive adsorption, pepsin and high-concentration bile salt (5000 mg/L, above critical micelle concentration) solubilized phenanthrene (3 and 30 times of the water solubility, respectively), thus substantially reducing phenanthrene adsorption on CNTs. Furthermore, 43-



69% of phenanthrene was released from CNTs after desorption in the simulated gastric and intestinal fluid at low bile salt concentration while 53-86% was released in the gastric and intestinal fluid at high bile salt concentration. These findings suggest that the release of residual HOCs from CNTs could be enhanced by biomolecules in the digestive tract, thus increasing the bioaccessibility of adsorbed HOCs and possibly the overall toxicity of HOCs-associated CNTs. Therefore, it is important that CNTs used for wastewater treatment plants would be processed to remove adsorbed HOCs and other contaminants before disposal (Wang et al., 2011c).

The second-most important human exposure pathway for CNTs after digestion is inhalation (e.g., following waste incineration). Before entering alveolar cells and exhibiting toxicity, CNTs initially encounter pulmonary surfactant consisting of lipids and proteins which cover the thin aqueous lining layer. The concern is that adsorbed HOCs may be released from the inhaled CNTs when they are in contact with pulmonary surfactant. A passive dosing method (avoiding centrifugation) was employed to investigate the effects of pulmonary surfactant on PAHs adsorption by and desorption from CNTs. This method allowed separating the contribution of competitive adsorption from that of solubility enhancement in the overall suppression of PAHs adsorption by the surfactant. The results demonstrated that when phenanthrene-adsorbed CNTs enter the respiratory tract, phenanthrene can be desorbed due to both solubilization and competition. Considering that the concentration of pulmonary surfactants covering the alveoli is higher than the tested concentrations suggests that the suppression of phenanthrene adsorption to CNTs when entering the respiratory tract may considerably increase the bioaccessibility of PAHs. Bioaccessibility might increase even further after reaching the blood circulation system. These results might imply a serious health risk of PAHs-associated CNTs (Zhao et al., 2012).

In contrast with HOCs, many pesticides and antibiotics are ionizable in the environmentally-relevant pH range, similar to DOM itself. The pH-dependent adsorption of benzoic acid, phthalic acid, and 2,6-dichloro-4-nitrophenol model compounds by hydroxylated, carboxylated, and graphitized CNTs was investigated (Li et al., 2013). Adsorption was contributed by formation of a negative charge-assisted H-bond between a carboxyl group on the solute and a phenolate or carboxylate group on the surface having a comparable pK_a . This exceptionally strong H-bond is depicted as $(RCO_2 \cdots H \cdots O - CNT)$. Formation of such bond helps overcome the unfavorable free energy of proton exchange with water, and results in an upward shift in the pK_a in the adsorbed state compared to the dissolved state. These findings provide new understanding of the interactions between ionizable organic compounds and carbonaceous surfaces, with implications



for noncovalent derivatization of CNTs, fate of ionizable pollutants, and associations of DOM with CNTs and other carbonaceous materials in the environment.

CNTs, organic contaminants and DOM can co-occur in the environment. The effect of the occurrence of co-contaminants, as well as of co-introduction of DOM, on the adsorption of carbamazepine to single-walled CNTs was evaluated (Lerman et al., 2013). Strong competition with bisphenol A and no effect of phenanthrene on adsorption of carbamazepine to CNTs were obtained. Presence of DOM in concentration similar to reclaimed wastewater caused sharp decreases in carbamazepine adsorption to CNTs. The effect of isolated hydrophobic fractions of DOM showed similar reducing effects on carbamazepine adsorption, in contrast with the isolated hydrophilic DOM fractions which did not affect carbamazepine adsorption to the CNTs. Additional experiments demonstrated a significantly higher binding affinity of carbamazepine to the hydrophobic neutral DOM fraction than to the hydrophobic acid fraction, suggesting that the latter could compete more effectively with carbamazepine for CNT adsorption sites, while the former could more effectively reduce carbamazepine adsorption via interactions in the solution. The net effect of co-introducing DOM and bisphenol A in reducing carbamazepine adsorption was higher than the effects caused by the individual components.

Li et al. (2014) further investigated the effects of CNT type and solution pH on the mechanisms involved in the adsorption of ciprofloxacin, a polar, ionizable antibiotic with marked pH-dependent solubility and lipophilicity. Highly nonlinear isotherms of ciprofloxacin were observed, indicating the highly heterogeneous site energy distribution on CNTs. The adsorption of ciprofloxacin on CNTs was greatly affected by pH. Hydrophobic interactions controlled zwitterionic ciprofloxacin adsorption while electrostatic interactions were the dominant mechanism for ionic ciprofloxacin adsorption. Under all pH conditions, single-walled CNTs had the highest adsorption for ciprofloxacin due to its largest surface area among all CNTs. The π - π electron donor-acceptor interactions were the reason for higher adsorption on hydroxylized than on carboxylized CNTs. For single-walled CNTs, ciprofloxacin adsorption was thermodynamically favorable and endothermic, associated with entropy driven process, while the reverse process occurred for graphitized multi-walled CNTs. The irreversibility of desorption hysteresis followed the order of single-walled > hydroxylized > graphitized multi-walled > carboxylized CNTs. The rearrangement of bundles or aggregates of CNTs and possible formation of covalent bonds between -OH and -COOH groups may be the reason for desorption hysteresis. Desorption of antibiotics from CNTs may lead to potential exposure, particularly under changing environmental conditions such as temperature and pH.



Details of Cooperation

The proposed research was conducted in close collaboration between the two PIs. Dr. Chefetz and Dr. Xing have met a few times during the project for active discussions and planning for optimal flow of the project. The research groups of Drs. Chefetz and Xing were mutually engaged in sorption-desorption experiments with natural as well as artificial systems, yielding complementary insights regarding the fate of CNTs in the environment and their effects on pollutants' fate. This joint work resulted in few (3) joint publications. Samples were exchanged between the two groups for analyses. The two groups were actively communicating for data analyses and the writing of scientific papers. In addition to the active and fruitful collaboration of the PIs in this project, students from the two groups communicated via emails to examine lab procedures, share and analyze experimental data.

List of Publications

Published articles

1. Wang, Z., Chen, J., Sun, Q. and Peijnenburg, W. J. G. M. 2011a. C60-DOM interactions and effects on C60 apparent solubility: a molecular mechanics and density functional theory study. *Environment International* 37, 1078-1082.
2. Wang, X., Shu, L., Wang, Y., Xu, B., Bai, Y., Tao, S. and Xing, B. 2011b. Sorption of peat humic acids to multi-walled carbon nanotubes. *Environmental Science & Technology* 45, 9276-9283.
3. Wang, Z., Zhao, J., Song, L., Mashayekhi, H., Chefetz, B. and Xing, B. 2011c. Adsorption and desorption of phenanthrene on carbon nanotubes in simulated gastrointestinal fluids. *Environmental Science & Technology* 45, 6018-6024.
4. Lin, D., Tian, X., Li, T., Zhang, Z., He, X. and Xing, X. 2012. Surface-bound humic acid increased Pb²⁺ sorption on carbon nanotubes. *Environmental Pollution* 167, 138-147.
5. Zhao, J., Wang, Z., Mashayekhi, H., Mayer, P., Chefetz, B. and Xing, B. 2012. Pulmonary surfactant suppressed phenanthrene adsorption on carbon nanotubes through solubilization and competition as examined by passive dosing technique. *Environmental Science & Technology* 46, 5369-5377.
6. Mashayekhi, H., Ghosh, S., Du, P. and Xing, B. 2012. Effect of natural organic matter on aggregation behavior of C60 fullerene in water. *Journal of Colloid and Interface Science* 374, 111-117.
7. Li, X., Pignatello, J. J., Wang, Y. and Xing, B. 2013. New insight into adsorption mechanism of ionizable compounds on carbon nanotubes. *Environmental Science & Technology* 47, 8334-8341.
8. Lerman, I., Chen, Y., Xing, B. and Chefetz, B. 2013. Adsorption of carbamazepine by carbon nanotubes: effects of DOM introduction and competition with phenanthrene and bisphenol A. *Environmental Pollution* 182, 169-176.



Final Scientific Report

9. Li, H., Zhang, D., Han, X. and Xing, B. 2014. Adsorption of antibiotic ciprofloxacin on carbon nanotubes: pH dependence and thermodynamics. *Chemosphere* 95, 150-155.
10. Polubesova, T. and B. Chefetz. 2014. DOM-affected transformation of contaminants on mineral surfaces: A review. *Critical Reviews in Environmental Science and Technology* 44:223-254.

Articles in preparation for submission

1. Zhao, Q., Yang, K., Chefetz, B., Zhao, J., Mashayekhi, H., and Xing, B. Dispersing functionalized carbon nanotubes by small polar aromatic organic molecules.

Student theses

1. Ilia Lerman. M. Sc. Thesis submitted to the Hebrew University of Jerusalem. "Adsorption of Carbamazepine by Carbon Nanotubes: Effects of DOM Introduction and Competition with Phenanthrene and Bisphenol A"

Conference Presentations

1. Xing, B. "Uptake, accumulation and translocation of engineered nanomaterials in agricultural crops." Tampa, FL, November 3-6, 2013. Abstract #: 294-8. ASA/CSSA/SSSA 2013 International Annual Meetings.
2. Xing, B. "Engineered nanoparticles in the environment: Potential risks and challenges." Cincinnati, OH, October 21-24, 2012. Abstract #: 86-7. ASA/CSSA/SSSA 2012 International Annual Meetings.
3. Xing, B. "Naturally occurring and engineered nanoparticles", the 16th Conference of International Humic Substance Society (September 9-14, 2012, Hangzhou, China).
4. Xing, B. "Environmental behavior and implications of engineered nanomaterials." The 15th International Humic Science & Technology Conference, March 14-16, 2012. Boston, MA.
5. Xing, B. "Environmental fate and toxicity of manufactured nanoparticles," The 6th International Symposium of Interactions of Soil Minerals with Organic Components and Microorganisms", France, June 26 – July 1, 2011.
6. Xing, B. "Dissolved organic matter influences the environmental behavior and toxicity of engineered nanomaterials." The 14th International Conference of Humic Science & Technology, Boston, MA. March 9-11, 2011.
7. Xing, B. "Environmental and colloidal behavior of engineered nanoparticles." International Symposium of Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone, Hangzhou, China, October 10-14, 2009
8. Chefetz, B., A. Oren, H. Haham and R. Navon. 2013. "The effects of exogenous DOM on binding reversibility of polar organic pollutants" 245th American Chemical Society National Meeting & Exposition. April 7-11, New Orleans, LA.



Final Scientific Report

9. Chefetz, B. and A. Oren. 2011. "Interaction of dissolved organic matter with mineral soil matrices: sorption-desorption and fractionation" ASA-CSSA-SSSA International Annual Meeting, October 16-19, San Antonio, TX, USA.
10. Chefetz, B., I. Lerman and Y. Chen. 2012. "Adsorption of contaminants of emerging concern by carbon nanotubes: Influence of dissolved organic matter". The 16th Meeting of the International Humic Substances Society: Functions of Natural Organic Matter in Changing Environment. September 9-14, 2012. Hangzhou, China.